

LAWRENCE LIVERMORE NATIONAL LABORATORY

Characterization of Uranium Particles Produced via Pulsed Laser Deposition

S.C. Glade, T.W. Trelenberg, J.G. Tobin, and A.V. Hamza

submitted 11/2003

2003 MRS Fall Meeting Symposium Proceedings

Boston, MA

December 1-5, 2003

Symposium DD: Actinides—Basic Science, Applications, and Technology

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Characterization of Uranium Particles Produced via Pulsed Laser Deposition

S.C. Glade, T.W. Trelenberg, J.G. Tobin, and A.V. Hamza
Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory
Livermore, CA 94551, U.S.A.

ABSTRACT

We have constructed an experimental apparatus for the synthesis (via pulsed laser deposition) and analysis of nanoparticles and thin films of plutonium and other actinides. *In-situ* analysis techniques include x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). Also, the oxidation kinetics and the reaction kinetics of actinides with other gaseous species can be studied with this experimental apparatus. Preliminary results on depleted uranium are presented.

INTRODUCTION

Of all the actinides, plutonium is possibly one of the most challenging to study. Computational modeling of plutonium, with its many unique and theoretically unexplained properties [1], is currently ongoing (eg., [2], [3], and [4]). To develop the predictive capability of these models, experimental benchmarks are needed. For electronic structure models, the most direct comparison of models with experiment is provided through photoelectron spectroscopy.

To this end, we have constructed an experimental apparatus for the synthesis and analysis of nanoparticles and thin films of plutonium and other actinides [5, 6]. It is suspected that the electronic properties of plutonium vary with particle size; by measuring the electronic structure evolution as it varies with particle size, we hope to determine the correlation and spin contributions to the electronic structure.

Initial experiments are being performed with depleted uranium. Depleted U has a lower activity and toxicity than plutonium, allowing us to more easily test the different components of the experimental apparatus. In this paper, we present initial results on depleted U.

EXPERIMENTAL DETAILS

The driving design requirements of the experimental apparatus were (1) that the total amount of actinide used must be minimized and that (2) the vacuum vessels themselves serve as containment vessels. A detailed description of the experimental apparatus is given in Ref. 6.

Briefly, nanoparticles of an actinide are deposited onto a 13 x 13 mm substrate (Si wafers and Au-coated Si wafers) via pulsed laser deposition in a sample preparation chamber. The actinide target used for deposition is small (< 25 mg), and the laser used is a Nd:YAG pulsed laser (10 Hz pulse rate, 5 ns pulse duration) operating in the 532 nm (green) second harmonic. The laser spot size on the target is $\sim 0.009 \text{ cm}^2$, giving a power density of $\sim 0.3 \text{ GW/cm}^2$ for the ablation of U. After production of a specimen, the substrate is transferred *in-situ* to an analysis chamber. Here, the actinide deposit is analyzed using XPS, UPS, STS, and STM. In order to

insure that the samples do not oxidize too rapidly, pressure in the chamber must be kept in the 10^{-10} to 10^{-11} Torr range.

RESULTS

Depleted U was first deposited on a silicon substrate in January 2003. The sample was oxidized, as evidenced by the large O 1s peak and the UO_x 4f peaks seen in XPS. The pressure in the experimental apparatus was in the low 10^{-9} torr range. This initial experiment proved the experimental and design concepts used in the experimental apparatus, but more work was needed to obtain unoxidized specimens.

Through the installation of new vacuum pumps giving pressures of $\sim 3 \times 10^{-10}$ torr throughout the experimental apparatus and, probably more importantly, better cleaning of the surface of the depleted U target before ablation of a specimen, we have deposited unoxidized depleted U on a Au-coated Si substrate. Due to bake-out of the sample preparation chamber before the production of specimens, the surface of the depleted U target oxidizes. The cleaning procedure consists of ablating this oxide layer onto a silicon substrate before ablating a specimen. A neutral density filter (optical density 0.10, 79.43% transmittance) is now placed in the laser beam path after the cleaning ablation to reduce the outer-wings of the beam profile below the ablation threshold for the production of a specimen; we believe that this is helping to obtain unoxidized specimens by ablating only unoxidized material during specimen preparation. Also, by increasing the number of laser pulses used in the cleaning process, we believe that we are more completely removing the oxide layer, which is helping to obtain unoxidized specimens.

Figure 1 shows the XPS U 4f peaks. As the specimen sits in the experimental apparatus, it oxidizes, as shown by the UO_x peaks increased intensity with time. The oxide peak does not start becoming evident until ~ 4 h after ablation, giving us this much time to analyze a newly prepared specimen.

Figure 2 shows the XPS at the Fermi level of the same specimen. The peaks at 2.5 eV and 6.5 eV binding energy are from Au. A peak due to the U 5f electrons appears at the Fermi edge in the U spectrum, in contrast to the clean Au spectrum. The Au and U spectra in figure 2 compare well with spectra in Ref. [7]. The peak at the Fermi edge decreases in intensity with time due to the oxidation of U.

A quantitative analysis of the Au 4d and the U 4f peaks shows that the U coverage on the Au substrate (the same specimen discussed above) is low ($< 20\%$). This low coverage was confirmed via *ex-situ* SEM of the specimen. The U particles have sizes ranging from 50 nm to 2 μm . Most of the U particles have a spherical shape, indicating that the U was molten prior and then solidified prior to deposition onto the Au substrate. Other U particles have more oblong shapes, possibly indicating that the U was still molten when it came into contact with the Au substrate and wetted the substrate prior to solidification.

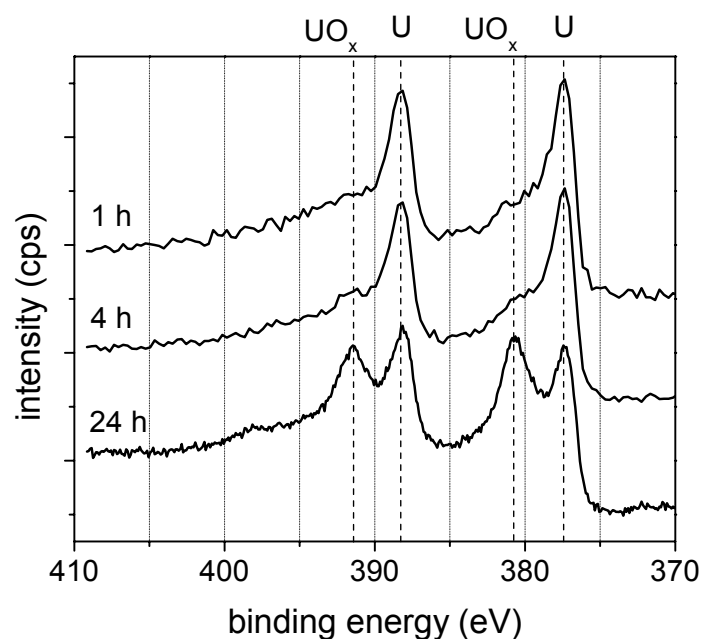


Figure 1. XPS (1253.6 eV, Mg K α) of the U 4f peaks at various times following initial specimen preparation. Note the growth of the oxide peaks with time.

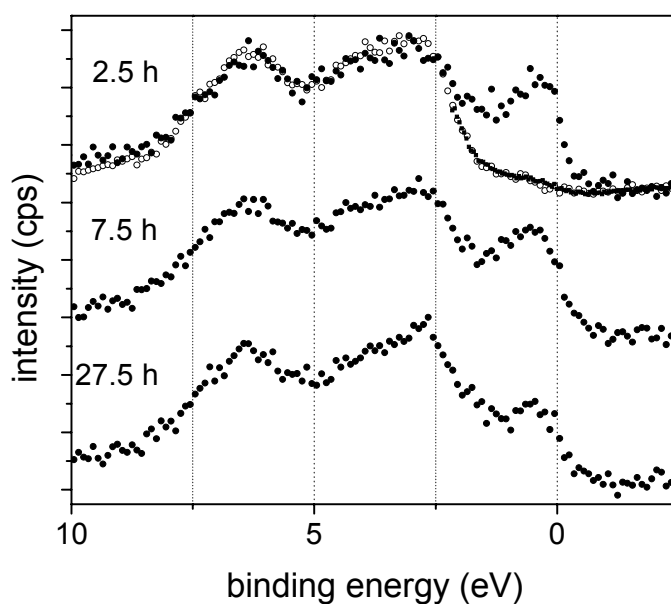


Figure 2. XPS (1253.6 eV, Mg K α) of the Fermi edge of U deposited onto Au coated Si substrate at various times following initial specimen preparation. Also plotted with the 2.5 h data is a spectrum from clean Au (○) and a high resolution spectrum of Au at the Fermi edge (■).

SUMMARY

We have demonstrated the capability of obtaining metallic actinides with a new experimental apparatus. Further testing and benchmarking of the apparatus will proceed with depleted uranium specimens produced via pulsed laser deposition, and then we plan to perform experiments on plutonium.

ACKNOWLEDGEMENTS

The authors acknowledge the scientific and design support of Dr. Mehdi Balooch and the design support of Alan Wardlow. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

REFERENCES

1. S.S. Hecker, MRS Bull. **26**, 667 (2001).
2. W.A. Harrison, *Phys. Rev. B* **64**, 235112 (2001).
3. S.Y. Savrasov, G. Kotliar, and E. Abrahams, *Nature* **410**, 773 (2001).
4. P. Soderlind, *Europhys. Lett.* **55**, 525 (2001).
5. S.C. Glade, T.W. Trelenberg, J.G. Tobin, P.A. Sterne, and A.V. Hamza in *Plutonium Futures-The Science*, ed. G.D. Jarvinen (AIP Conf. Proc. **673**, Melville, NY, 2003) pp. 148-149.
6. T.W. Trelenberg, S.C. Glade, T.E. Felter, J.G. Tobin, and A.V. Hamza, "A Novel Instrument for the Investigation of the Nanostructure of Pu and other Actinides," accepted to *Rev. of Sci. Inst.*, 10/2003.
7. W.-D. Schneider and C. Laubschat, *Phys. Rev. B* **23**, 997 (1981).